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Comparison of wastewater-associated contaminants in the bed sediment of Hempstead Bay, New York, before and after Hurricane Sandy

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ABSTRACT

Changes in bed sediment chemistry of Hempstead Bay (HB) have been evaluated in the wake of Hurricane Sandy, which resulted in the release of billions of liters of poorly-treated sewage into tributaries and channels throughout the bay. Surficial grab samples (top 5 cm) collected before and (or) after Hurricane Sandy from sixteen sites in HB were analyzed for 74 wastewater tracers and steroid hormones, and total organic carbon. Data from pre- and post-storm comparisons of the most frequently detected wastewater tracers and ratios of steroid hormone and of polycyclic aromatic hydrocarbon concentrations indicate an increased sewage signal near outfalls and downstream of where raw sewage was discharged. Median concentration of wastewater tracers decreased after the storm at sites further from outfalls. Overall, changes in sediment quality probably resulted from a combination of additional sewage inputs, sediment redistribution, and stormwater runoff in the days to weeks following Hurricane Sandy.

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1. Introduction

The damage to wastewater-treatment infrastructure in the northeast United States caused by Hurricane Sandy during October 2012 has been well documented (Kenward et al., 2013; City of New York, 2013; Federal Emergency Management Agency, 2013). Sewage treatment plants (STPs) and associated transfer (pumping) stations on the south shore of Long Island, New York, were hit particularly hard because of their proximity to the coast, a low-gradient topography, and the high storm tide experienced in Nassau and Suffolk Counties (Schubert et al., 2015). Failed wastewater treatment infrastructure resulted in billions of liters of untreated and partially-treated sewage being discharged into Hempstead Bay (HB), which occurred as water levels surpassed the Federal Emergency Management Agency's 100-year flood zone for the area. Hurricane Sandy also caused the redistribution of bed sediment within the bays (Swanson et al., in press) and overwash from the barrier islands, resulting in significant changes to the bay bottom with respect to particle-size and associated legacy contaminants distribution. More details regarding the storm tide impacts and general chemical distribution in sediment of the New York and New Jersey coastal regions can be found in U.S. Geological Survey reports on data collected specific to impacts of Hurricane Sandy (Fischer et al., 2015; Schubert et al., 2015) and other papers published as part of this Special Issue (Reilly et al., 2016–in this issue; Phillips et al., 2016–in this issue).

Hempstead Bay typically receives the majority of roughly 230 million liters per day of treated sewage effluent from two STPs—Bay Park STP (Bay Park, New York) at 200 million liters per day and Long Beach STP (Long Beach, New York) at 20 million liters per day, both of which discharge to Reynolds Channel from outfalls located 1 km apart. (Stormwater in the region is not treated at the STPs and discharges to the HB through direct runoff and storm drains.) However, for nearly 48 h following landfall of Hurricane Sandy, Bay Park STP plant was offline, with no primary or secondary treatment occurring. During this period, raw sewage and seawater that had backed up in the 2400 km of sewers flooded streets and homes. This effluent-laden water was eventually transferred directly to Mill River and three other tributaries of HB from selected low-lying manholes using auxiliary pumps (Swanson et al., in press), and resulted in the release of 380 million liters of untreated sewage (Kenward et al., 2013). Several days after the storm had passed, partial treatment (i.e., primary with some secondary treatment) was restored at Bay Park STP; however, a total of 8.7 billion liters of poorly-treated sewage were discharged to either East Rockaway Channel from the Bay Park STP auxiliary outfall adjacent to the plant (just south of Mill River) and, depending on the tides, from the normal outfall location in Reynolds Channel for over the next 44 days (Hydroqual, 2013; Kenward et al., 2013). The timing of discharges and some of the effects resulting from the use of the auxiliary outfall, including turbidity spikes, reduced DO, and reduced salinity,

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were observed. Long Beach STP was also severely damaged, and it is not clear how much untreated sewage discharged from that plant to the adjacent waters during the storm. However, public works officials managed to avoid continued discharge of poorly-treated sewage by creating an expansive network of public portable restrooms until their STP and pumping system could be repaired.

During normal STP operations, treatment of wastewater results in the partial to complete removal of many natural and anthropogenic compounds, while other compounds pass through with minimal removal depending on the level of treatment (Furtula et al., 2012; Phillips et al., 2012). Insufficient treatment (resulting from damage caused by a natural disaster, for example) degrades water quality of the receiving waters and can introduce contaminants that can adversely affect the ecosystem to which effluent is discharged (Amaral-Zettler et al., 2008; Farre et al., 2002). Diagnostic information about the level of treatment of sewage inputs can be obtained by looking at the composition of sewage-derived compounds (Phillips et al., 2012; Li and Brownawell, 2010). Compounds associated with wastewater typically present in the sediments around STP outfalls include fragrances galaxolide and tonalide, which are not as well removed during treatment (Phillips et al., 2012; Sumner et al., 2010). Thus, these wastewater tracers would be expected to be present in sediment even without raw sewage inputs. On the other hand, compounds such as skatole (an odor-causing compound found in untreated sewage) are typically well-removed during secondary treatment (Phillips et al., 2012; Rudolfs and Chamberlin, 1932) and would be introduced at higher concentrations during STP failure than under normal operations. Thus, a significant increase in the concentration of skatole in the bed-sediment samples collected after Hurricane Sandy would suggest the influence of poorly-treated sewage.

Bed sediment characteristics (such as concentration of total organic carbon and grain size distribution) throughout HB were documented prior to Hurricane Sandy, and changes observed following the storm were attributed to the redistribution of sediment (Swanson et al., in press). Particle size and total organic carbon (TOC) analyses on cores collected at select sites before and again after Hurricane Sandy indicate changes in the TOC concentrations and grain size distribution resulting from combinations of scouring and the deposition of sand. In addition, the newly deposited sand was found to contain traces of recently-discharged sewage based on the ratios and concentrations of quaternary ammonium compounds (QACs) (Swanson et al., in press; Doherty, 2013). Further, a modeling exercise conducted by Swanson et al. (in press) illustrates the dispersion of sewage from the primary and auxiliary outfalls for the Bay Park STP in the hours following plant failure and emphasizes tidal influences in the channels and lack of flushing in the back bays.

Comparing concentrations ratios of compounds related to wastewater has been used to identify potential sources of wastewater in sediment. Ratios of concentrations of 3-beta-coprostanol to cholesterol have been used to distinguish human inputs of steroid hormones from those of wildlife (Furtula et al., 2012; Marvin et al., 2001; Grimalt et al., 1990); ratios greater than 0.2 have been argued to indicate sewage sources. Concentrations of polycyclic aromatic hydrocarbons (PAHs), including ratios of anthracene to phenanthrene and fluoranthene to pyrene, have been used to distinguish petroleum spills from combustion as sources of PAHs in sediment. The ratios of PAH concentrations have also been used to identify a potential sewage source. Recently, concentration ratios of a variety of QACs, a broad class of ionic surfactants, have been used to delineate the areal extent of impact from the Bay Park STP effluent (Doherty, 2013). The ratios of QACs found in sediment are based on the level of treatment and removal efficiencies at the STP and their degradation rates following discharge. The detection of QACs throughout HB indicates sewage-affected sediments were distributed over 5 km from the Bay Park STP outfall in Reynolds Channel in a 2010–2012 study (Doherty, 2013).

The purpose of this study was to assess the extent to which the bed-sediment chemistry in HB changed following Hurricane Sandy. This assessment was conducted by comparing the concentrations of wastewater tracers and steroid hormones in samples collected before and after the storm. This study presents the first post-Hurricane Sandy set of comprehensive wastewater-indicator and hormone data in the bed sediment chemistry of HB. It also serves as a baseline that can be used to compare with results from future sampling efforts.

2. Methods

2.1. Sample Network

Hempstead Bay (HB) is part of an estuary on the south shore of Long Island, New York, and consists of a series of smaller bays and channels including Hewlett Bay, Reynolds Channel, Brosewere Bay, Middle Bay and East Bay (Fig. 1). A network of sites established by Brownawell et al. at Stony Brook University School of Marine and Atmospheric Sciences (SoMAS) for studying QACs distribution (Doherty, 2013; Li and Brownawell, 2010) from 2010 to 2012 was reoccupied after Hurricane Sandy in February 2013. Sediment samples analyzed for this study were taken from archived split samples stored at SoMAS. Sixteen sites from this HB network (Fig. 1; Table S1) were chosen based on proximity to the Bay Park STP outfalls, availability of archived sediment, an understanding of hydrodynamics of the bays, and observed changes in bed-sediment characteristics (i.e., grain size distribution) resulting from Hurricane Sandy (Swanson et al., in press). Of the sites chosen: sufficient sample volumes were available from eight sites for pre- and post-storm comparisons, four of the remaining sites had only pre-storm samples available, and the last four sites had only post-storm samples available. Samples without matching pairs were analyzed to assess the range in concentrations of wastewater tracers and hormones in 2010–2012, and after the storm in early 2013. This assessment permitted pre- and post-storm comparisons to better describe the general conditions of HB and supplement the QACs data previously documented for these samples (Swanson et al., in press; Doherty, 2013).

2.2. Sample collection and handling

Samples in HB were collected by SoMAS and Town of Hempstead Conservation and Waterways using surficial grab samplers (Petite Ponar®) to collect the top 5 cm of bed sediment. Samples were immediately chilled and were frozen at −20 °C upon return to SoMAS (Doherty, 2013). In 2014, splits of the sediment samples were shipped on-ice directly to the USGS National Water Quality Laboratory in Denver, Colorado, for analysis of wastewater-indicator and hormone compounds.

(Note: Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.)

2.3. Analytical methods

Data presented in this article were generated using two standard methods for contaminants of emerging concern in soil and sediments. The USGS wastewater-indicator method (lab schedule 5433) tests for compounds often associated with sewage and stormwater runoff in sediment. The USGS hormone method (lab schedule 6434) tests for natural and synthetic hormones that can also be used as sewage tracers. The two methods have three compounds in common: cholesterol, 3-beta-coprostanol, and bisphenol A (BPA). A brief discussion of these methods is provided below, with more detail available in the Supplementary materials and the respective USGS method publications. The TOC analyses were conducted according to methods in Doherty (2013).

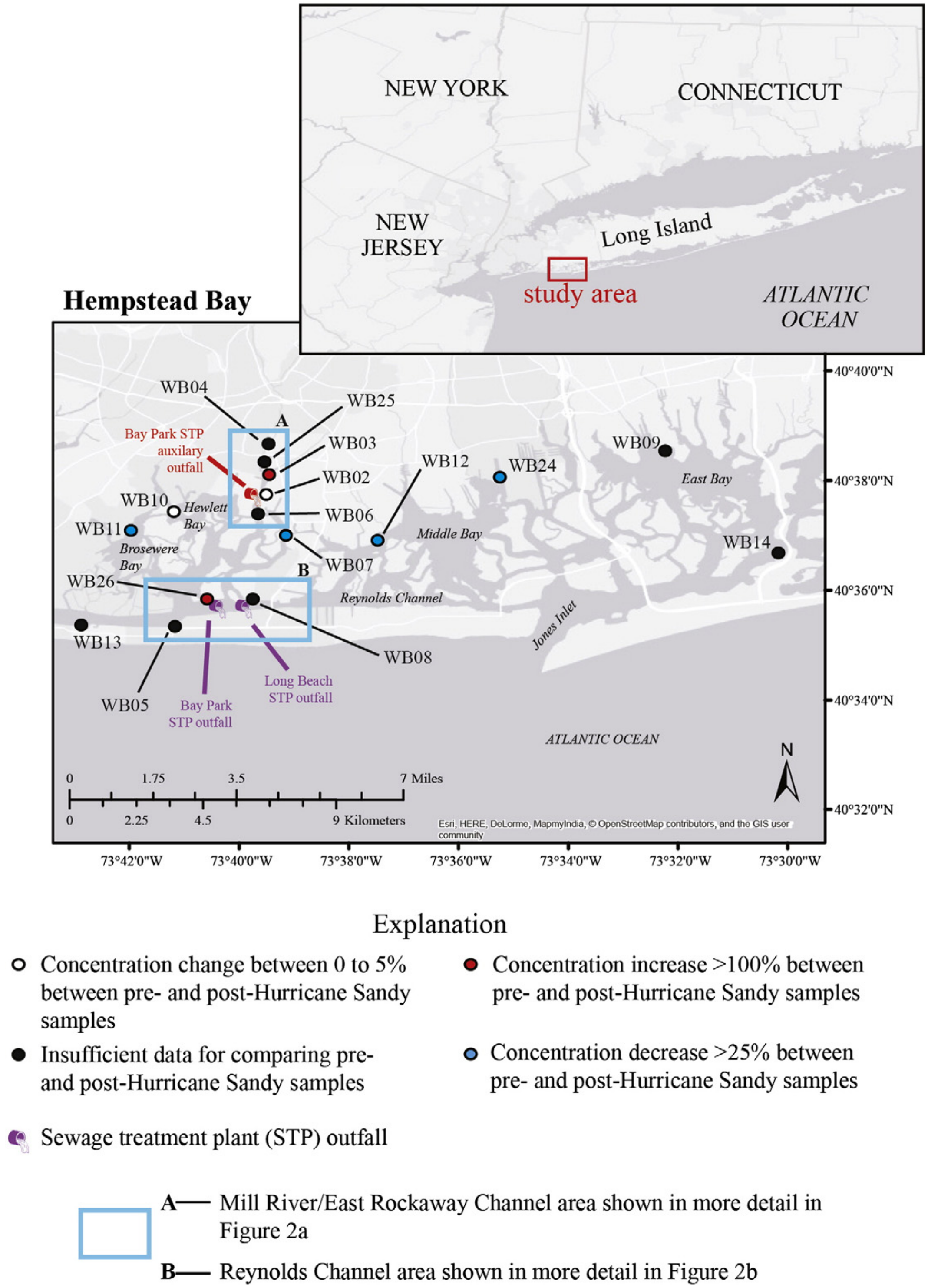

Fig. 1. Hempstead Bay bed sediment sample locations. Map of sites sampled in Hempstead Bay, New York, 2010–2013. For sites with samples collected pre- and post-Hurricane Sandy, sites are classified by change in concentrations between pre- and post-Hurricane Sandy conditions. Concentration increases (shown as sites with red dot) and concentration decreases (shown as sites with blue dot) are significant at the $p = 0.10$ level by rank test.

2.3.1. Wastewater-indicator method

Samples were analyzed for 57 compounds including surfactants, fragrances, antioxidants, antimicrobials, food additives, plastic components, industrial solvents, PAHs, plant and animal biochemicals, phosphate flame retardants, and high-use domestic pesticides (Table S2) using the wastewater-indicator method described by Burkhardt et al. (2006). Because this method largely focuses on compounds associated with wastewater, it is referred to as the USGS wastewater-indicator method in this paper. Analytes were extracted using isopropyl alcohol in a pressurized liquid extraction system and isolated using disposable solid-phase extraction cartridges. Concentrations were determined by capillary-column gas chromatography/mass spectrometry. The minimum sample volume was submitted for some samples and thus resulted in slightly higher minimum reporting levels for some compounds. Reporting limits for this method range from 10 to >100 μg/kg. Additional details can be found in the Supplementary materials.

2.3.2. Hormone method

The USGS hormone analytical method was used to analyze samples for 20 compounds, including nine natural and synthetic estrogens, six androgens, two progestins, two sterols abundant in wastewater (plant and animal biochemicals), and estrogen-mimicking BPA (Table S3). This method, referred to as the hormone method, is largely based on Foreman et al., 2012. Extraction was performed using a pressurized liquid extraction cell. Compounds were then derivatized using 500 μL of activated *N*-methyl-*N*-trimethylsilyl trifluoroacetamide (MSTFA) derivatization reagent and analyzed by gas chromatography/tandem mass spectrometry as described by Foreman et al. (2012). The minimum sample volume was submitted for some samples and thus resulted in slightly higher minimum reporting levels for some compounds. Reporting limits for this method range from 0.10 μg/kg (for most steroid hormones) to 25 μg/kg for cholesterol and 3-beta-coprostanol. Additional details can be found in the Supplementary materials. (Note: For this study, cholesterol, 3-beta-coprostanol, and BPA data reported from the hormone method were used for statistics because of better method performance for these compounds compared to the wastewater-indicator method—cholesterol, 3-beta-coprostanol, and BPA data from both methods are reported in Tables S2 and S3.)

2.3.3. Total organic carbon method

Samples were analyzed for total organic carbon (TOC) through the use of a Carlo_Erba 1108 CHNS Analyzer following acidification with 0.1 M hydrochloric acid. The analyzer was calibrated using sulphanilamide and samples were instrument-blank corrected. Precision of analysis was determined on a reference Long Island Sound sample with relative standard deviation for organic carbon of 2%. Further details on the TOC method are available in Doherty (2013).

2.4. Quality assurance and quality control

Samples were collected by SoMAS and Town of Hempstead using the same of type of equipment and similar techniques as the USGS used for the regional reconnaissance study following Hurricane Sandy (Phillips et al., 2016–in this issue; Fischer et al., 2015). Quality assurance and quality control (QA/QC) data for samples analyzed for this study are limited because of the limited amounts of archived sediment available. Therefore, the summary of QA/QC results for the USGS wastewater-indicator and hormone methods presented in the QA/QC and Supplementary materials sections of Phillips et al. (2016–in this issue), which include analysis results for field replicate, lab blank, and spike samples, can be used to infer extent of data variability in samples used for this study. Field replicate samples for the wastewater-indicator and hormone methods included two independent samples collected at the same location in the field but analyzed separately.

For the regional reconnaissance study, six field replicate samples were analyzed using the wastewater-indicator and hormone methods. Replicate analysis by the wastewater-indicator method yielded 77 paired analyte concentration comparisons (with detections in both samples) and 22 unpaired analyte comparisons (with a detection in only one of the two samples). A median relative percent difference (RPD) for these replicates was 27%, with most (90%) of the replicates having RPDs of 100% or less. Replicate analysis using the hormone method yielded 23 paired concentration comparisons and seven unpaired comparisons. A median RPD for these analyses was 31%, with most (90%) of the differences being 80% or less (Fischer et al., 2015).

2.5. Data analysis

Because the concentrations of analytes in different sediments are not normally distributed, statistical methods are largely based on non-parametric methods typically used for the interpretation of water-quality data (Helsel and Hirsch, 2002) and are more robust than parametric approaches for these types of data. Statistical analysis include analysis of percent change using the non-parametric sign test, and Spearman correlations and locally weighted scatterplot smoothing (LOESS) smooth lines to assess relations among the variables (Helsel and Hirsch, 2002). Some of the data used for calculations were qualified as estimated ("E") (Tables S2 and S3) because concentrations were either quantified below the minimum reporting limits or because of matrix interference (a broader discussion of the reason for estimating values can be found in Childress et al. [1999]). For the analysis presented in this paper, interpretations are based on concentrations above the minimum reporting limit, generally limiting the effect of greater variability present for lower concentration values. Detailed discussion of the approaches used for data near reporting limits are given in Supplementary materials.

3. Results and discussion

Data used in this study for comparing concentrations of wastewater-related compounds in sediment collected before and after Hurricane Sandy are presented in the Supplementary materials (Tables S2–S4). Some of the most frequently detected compounds in this study (Table S5) were selected out of the 57 wastewater tracers to represent broad classes of compounds detected using the wastewater-indicator method: acetophenone, a personal care product with potential sources in nature, has strong correlations with other wastewater-indicator compounds detected in this study; skatole, a sewage-derived compound, is typically well-removed under normal STP operations and thus provides indication of untreated sewage inputs; and anthracene, a PAH, has a strong correlation with other wastewater tracers, specifically sewage. Anthracene was detected in 92% of samples, and had the fewest number of estimated concentrations of the five most-frequently detected PAHs. Concentrations of both androgen compounds and estrogen compounds were summed for the purposes of comparing total steroid hormone classes (i.e., total androgens and total estrogens) to wastewater compounds and TOC. Correlations between pre- and post-Hurricane Sandy sample data, ratios of hormones and PAHs, and summary statistics were all used to help better understand the changes in sediment chemistry in areas near damaged sewage treatment infrastructure in HB resulting from Hurricane Sandy.

3.1. Pre- and post-Hurricane Sandy sediment quality comparisons

Individual compounds with concentrations above the reporting limit from the following classes were compared in the pre- and post-Hurricane Sandy samples: wastewater tracers (Table S2); steroid hormones, plant and animal biomolecules, and BPA (Table S3); and TOC (Table S4). The percent changes were determined by calculating the difference in concentration between the pre- and post-storm samples divided by the pre-storm sample concentration. Percent changes were determined for each analyte. For example, the skatole concentration at WB03 (Fig. 2a) increased from 14 μg/kg in the pre-Hurricane Sandy sample to 47 μg/kg in the post-storm sample—a percent change of +240% (which happens to correspond to the median value for the site). This comparison is one of 24 made for WB03 that were then combined to get an overall distribution of percent changes. Other significant differences noted for WB03 include: acetophenone increased from 124 to 404 μg/kg (+230%), galaxolide increased from 23.0 to 77.9 μg/kg (+240%), *p*-nonylphenol increased from 518 to 3220 μg/kg (+520%), tonalide increased from 2.74 to 18.1 μg/kg (+560%), 4-*t*-octophenol increased from 12.8 to 76.9 μg/kg (+500%), and anthracene increased from 53.3 to 224 μg/kg (+320%). There were also no compounds from

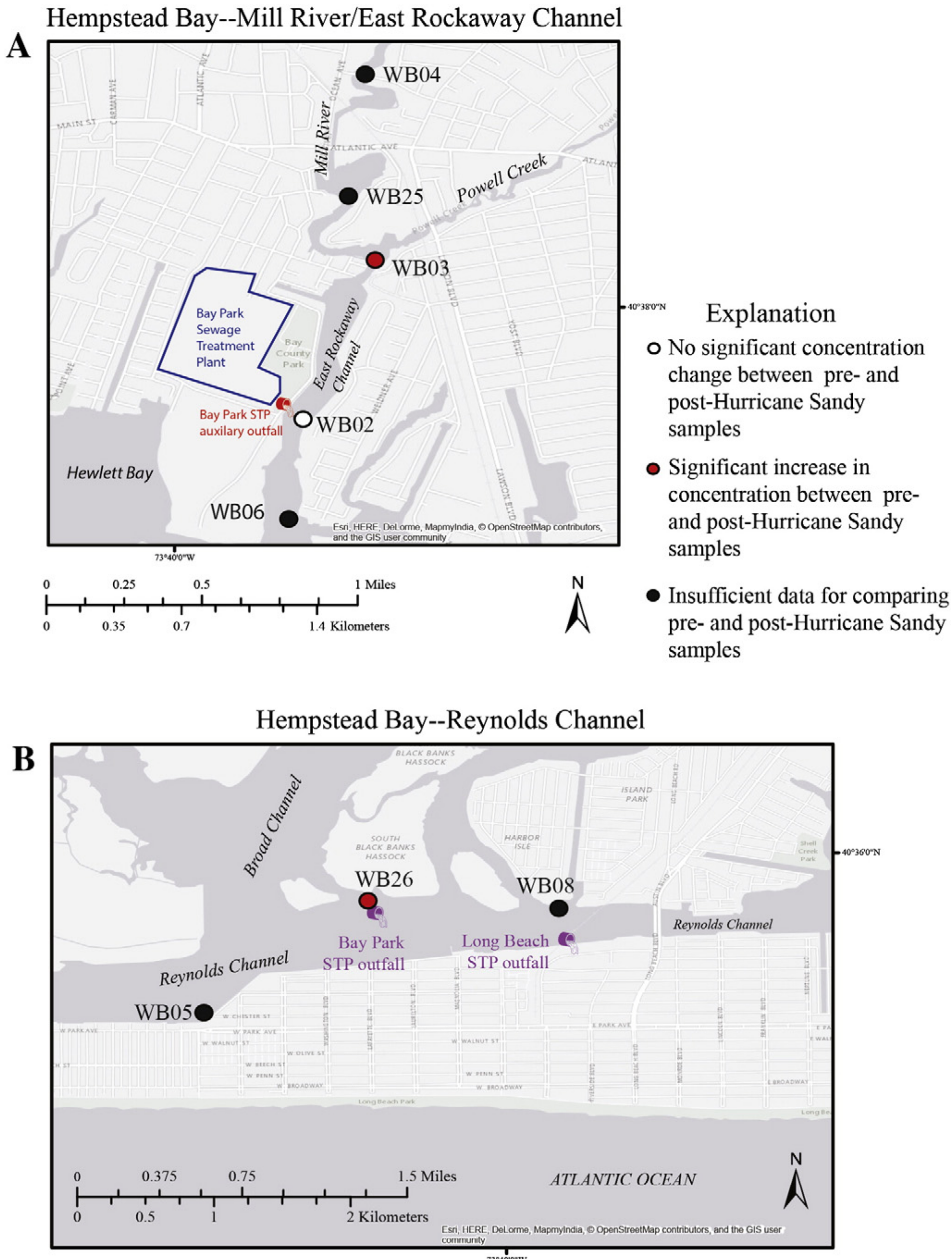

Fig. 2. a. Locations of samples collected in Mill River and East Rockaway Channel, 2010–2013. Percent Change For pre- and post-Hurricane Sandy samples is depicted with color points. Statistical comparison between pre and post sample concentrations based on non-parametric sign test; differences are significant at die $p < 0.05$ level. b. Locations of samples collected in Reynolds Channel, 2010–2013. Percent change for pre- and post-Hurricane Sandy samples is depicted with color points. Statistical comparison between pre- and post- sample concentrations based on non-parametric sign test: differences are significant at the $p < 0.05$ level.

the wastewater-indicator method that had concentrations lower in the post-storm WB03 sample (Table S2). Furthermore, the post-Hurricane Sandy WB03 sample contained some of the highest concentrations of individual wastewater tracers in the region (generally in the 90th percentile when compared across pre- and post-storm samples), while concentrations in pre-Hurricane Sandy samples at this site were typically around the median concentration for all the samples collected in HB.

The median percent change was also calculated for each site from all analytes with detections in both pre- and post-storm samples for a given compound and represents whether sediment at a site experienced significant changes in concentrations (at the $p < 0.05$ level). For example, the median percent change was positive at WB03, with concentrations of the compounds list above contributing to WB03 exhibiting the greatest positive changes of the eight sites with pre- and post-storm data (Fig. 3). On the other hand, there was no significant change in the concentrations of wastewater tracers at WB02, which is adjacent to the Bay Park STP auxiliary outfall (Fig. 2a), and concentrations at WB02 were generally less than those in either the before or after sample analyzed from WB03. The similarities in concentrations at site WB02 before and after Hurricane Sandy may be because of its location relative to the closest sewage inputs resulting from the storm. The auxiliary outfall discharged untreated sewage directly to the surface of the channel, rather than through dispersion from the bay bottom (as is done at the Bay Park STP main outfall). The partially-treated sewage would have lower density than seawater and thus could have been transported to the bay by currents rather than being deposited at

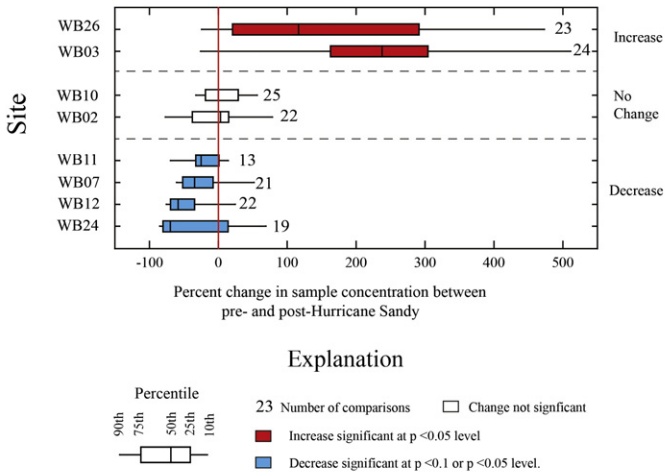

Fig. 3. Range of median percent changes for compounds detected in both pre- and post-Hurricane Sandy samples from Hempstead Bay, 2010–2013, analyzed using the wastewater-indicator, hormone, and total organic carbon methods. Concentration differences for sites WB03, WB26, WB07, and WBI2 are significant at $p < 0.05$; concentration differences for sites WB11 and WB24 are significant at the $p < 0.10$; concentration differences for sites WB02 and WBIO have $p > 0.10$. Statistical comparison between pre- and post-sample concentrations based on non-parametric sign test.

WB02. In contrast, untreated wastewater from emergency sewer line pumping was discharged to Mill River during and immediately following Hurricane Sandy probably became well-mixed within the water column. This could have contributed to the observed increase in concentration of wastewater tracers in sediment at WB03.

Sediment analyzed from site WB26 adjacent to the normal Bay Park STP outfall in Reynolds Channel (Fig. 2b) also experienced significant increases in the concentrations of wastewater tracers. The comparison was conducted using 23 compounds and had a median percent change of +116%. Differences worth noting for WB26 data include: 3-beta-coprostanol increased from 1100 to 2070 μg/kg (+88%), pyrene increased from 42.0 to 229 μg/kg (+450%), galaxolide increased from 31.4 to 65.6 μg/kg (+110%), indole increased from 80.0 to 159 μg/kg (+99%), anthracene increased from 11.9 to 70.4 μg/kg (+490%), and tributyl phosphate (a solvent and plasticizer) increased from 8.2 to 20 μg/kg (+140%). Of the 16 samples analyzed, WB26 is the only site where tributyl phosphate was detected and these occurrences were likely because of the proximity to the normal Bay Park STP outfall. There were also four observed decreases in concentrations in WB26 sediment from samples collected after Hurricane Sandy: triclosan (−20%); and *p*-nonylphenol, carbazole, and phenol, which were all detected at low concentrations in pre-storm samples were not detected in post-storm samples. The general increase in concentrations of wastewater tracers at WB26 was from the lower range (generally in the lower 25th percentile) to concentrations near the median. This may be the result of increased flushing of the tidal channel. However, as previously discussed, operations of the Bay Park STP was disrupted by Hurricane Sandy and the plant only minimally treated sewage for 44 days after the storm, which may have led to the observed increased concentrations of wastewater tracers at site WB26.

The five other sites from where sediment was collected before and after Hurricane Sandy were not immediately adjacent to the outfalls (Fig. 1). All but one of the five sites had concentrations of wastewater tracers that were lower after Hurricane Sandy (Fig. 3; Tables S2–S4). Summary statistics for WB07, WB10, WB11, WB12, and WB24, along with the three sites adjacent to the outfalls, are shown in Fig. 3. Of the four sites with significant decreases in wastewater tracer concentrations, sites in Hog Island Channel (WB07) and Brosewere Bay (WB11) experienced less of an overall change (median percent changes of −34% and −25%, respectively). Decreases in wastewater-tracer concentrations at the two sites in Middle Bay (WB12 and WB24) resulted in greater changes relative to other concentrations in the region (median percent changes of −58% and −70%, respectively). Significant differences at WB12 included: skatole decreased from 13.9 to 6.7 μg/kg (−52%), 3-beta-coprostanol decreased from 1490 to 754 μg/kg (−49%), and anthraquinone decreased from 94.1 to 38.1 μg/kg (−60%). Significant differences at WB24 included: anthracene decreased from 200 to 39.5 μg/kg (−80%), fluoranthene decreased from 698 to 105 μg/kg (−85%), phenanthrene decreased from 175 to 42.5 μg/kg (−76%), and pyrene decreased from 600 to 91.6 μg/kg (−85%). The most frequently detected wastewater tracers in WB24 were PAHs, and there were no detections of galaxolide or tonalide in the pre- or post-Hurricane Sandy samples. This indicates less sewage impact on the sediment in that area of Middle Bay, which correlates with the distance from the Bay Park STP outfalls and QACs data from Doherty (2013). Concentrations of wastewater tracers in samples collected from Hewlett Bay (WB10) did not change significantly between pre- and post-Hurricane Sandy samples (Fig. 3).

The range of concentrations at sites with a negative percent change varied, and may be the result of less contaminated sediment being redistributed during the storm. Wastewater tracer concentrations at WB07 for both the pre- and post-Hurricane Sandy samples were generally greater than the 75th percentiles. For example, acetophenone concentrations for site WB07 were above 350 μg/kg for samples collected before and after Hurricane Sandy, remaining among the highest for acetophenone in HB. Concentrations at WB11 were between the 25th and 50th percentiles for pre- and post-Hurricane Sandy samples. For site WB12, the concentrations after the storm were lower, decreasing from concentrations near the median to below the 25th percentile. For example, indole concentrations decreased from near median concentrations (120 μg/kg) to less than the 25th percentile (around 60 μg/kg). Similarly, concentrations of benzo[*a*]pyrene for WB24 samples decreased from the 75th percentile (310 μg/kg) to concentrations below median levels (43 μg/kg). Concentrations of wastewater compounds in samples from WB02 for pre- and post-Hurricane Sandy were generally lower than in other HB samples (except for WB14 [East Bay], which had the lowest concentrations of wastewater tracers in the study).

Although changes between pre- and post-Hurricane Sandy samples in the back bay region of HB (where sites WB10 and WB11 are located) did not reflect an increase in wastewater tracers, it has been suggested through hydrodynamic modeling that there is a residence time of about 10 days with respect to water flushing in and out from Reynolds Channel (Swanson et al., 2013). A longer residence time (relative to the rest of the bay) means contaminants discharged from Bay Park STP outfall (and East Rockaway Channel following the storm) generally have more time to mix and settle out. The occurrence and timing of particulate matter at this location correlate well with the turbidity readings shown in Fig. S1 of the Supplementary material, as well as the elevated (relative to other sites) wastewater tracer (including PAH) concentrations at WB10 in both pre- and post-Hurricane Sandy samples. For example, galaxolide concentrations for both samples from WB10 ranged from 72 to 79 μg/kg, which are both greater than the 75th percentile of all samples assessed for galaxolide in this study. Further, the concentration of skatole in the post-storm sample was significantly higher at WB10.

Additional sites within HB where sediment was collected either before or after Hurricane Sandy were analyzed for wastewater tracers to estimate a range of concentrations throughout the estuary. In samples taken from Mill River/East Rockaway Channel upstream and downstream of the Bay Park auxiliary outfall, concentrations of select wastewater tracers—acetophenone, skatole, and anthracene—were generally within the same order of magnitude in the pre-Hurricane Sandy samples (Fig. 4). After Hurricane Sandy, concentrations in sediment were elevated upstream at WB03, but appear relatively the same as concentrations in samples collected before Hurricane Sandy at WB02

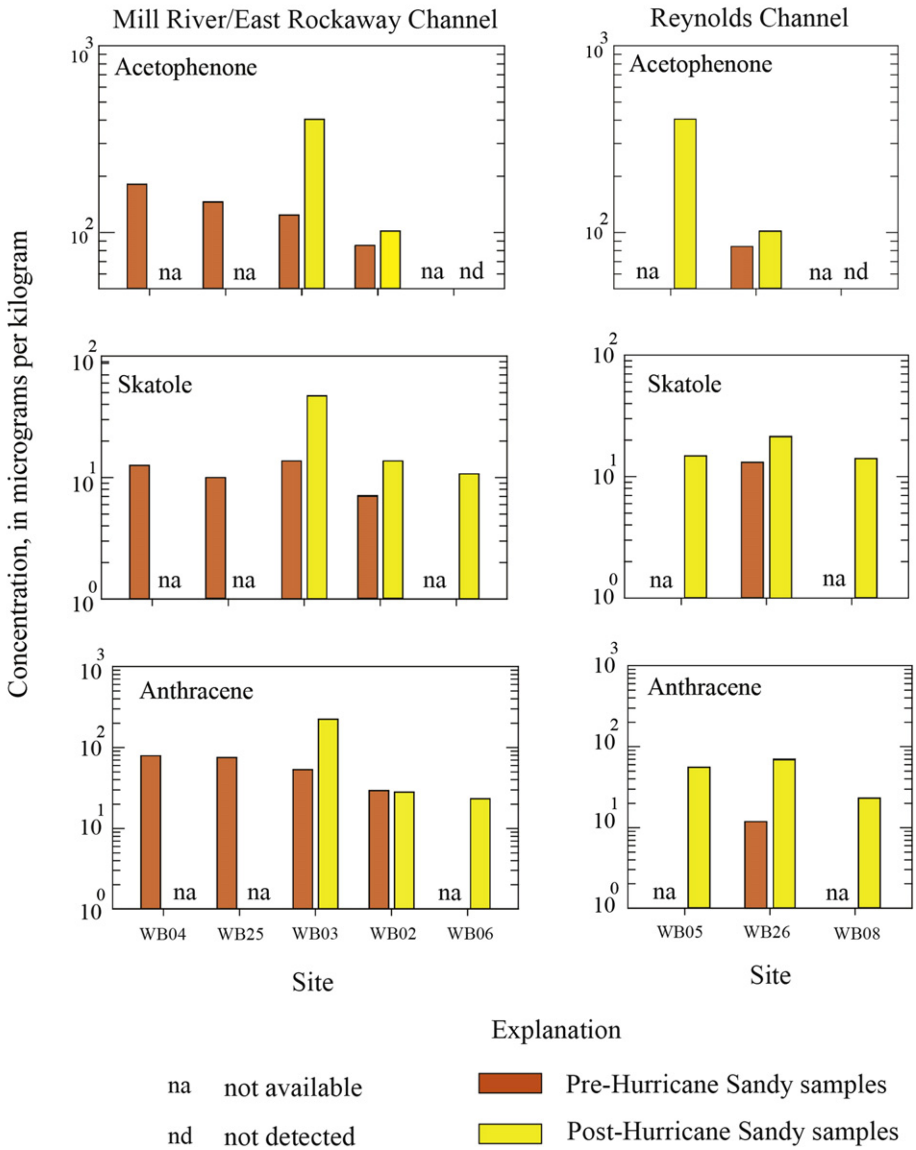

Fig. 4. Concentrations of acetophenone, skatole, and anthracene for pre- and post-Hurricane Sandy samples collected from Mill River/East Rockaway Channel and Reynolds Channel.

(as previously noted). Concentrations of skatole in sediment collected around the auxiliary outfall before Hurricane Sandy ranged from 7 to 14 μg/kg, and increased to 47 μg/kg at WB03 in its post-storm sample. Acetophenone concentrations ranged from 84 to 181 μg/kg in samples collected before Hurricane Sandy, and increased to 404 μg/kg at WB03. This increased sewage signal at WB03 was also correlated to increases in the concentrations of more conservative wastewater tracers, galaxolide and tonalide (Table S2), and may relate to the release of raw sewage into Mill River through the separated stormwater system immediately after Hurricane Sandy (Swanson et al., in press).

A concentration gradient for acetophenone and anthracene was observed in Mill River and East Rockaway Channel sediment samples collected before Hurricane Sandy (Fig. 4). The acetophenone gradient may exist because of previous discharges of poorly treated sewage from the Bay Park STP auxiliary outfall or sources of direct sewage inputs from illicit discharges or leaky sewer infrastructure near the shore or within the Mill River and Powell Creek watersheds. The anthracene (and other PAH) gradient could be explained by the increased contributions from road runoff that has been documented in Mill River north of Bay Park STP (Hydroqual, 2013).

Fig. 4 also shows concentrations of the wastewater tracers in Reynolds Channel site WB26 that were generally higher in post-Hurricane Sandy sediment samples (as previously mentioned). Concentrations at other sites east and west of the Bay Park STP outfall were at the same relative concentrations observed in Mill River post-Hurricane Sandy. However, with limited pre-Hurricane Sandy samples from Reynolds Channel available for this study, it is difficult to draw conclusions about changes in other areas of the channel. Data from studies conducted prior to Hurricane Sandy assessed other sewage tracers (i.e., QACs) to help distinguish between treated and untreated sewage releases, as well as the temporal and spatial distribution of the settling of sewage-related suspended solids (Doherty, 2013; Li and Brownawell, 2010). Comparing the wastewater tracer data in this study could provide additional diagnostics when compared to post-Hurricane Sandy concentration and ratio results from the QACs analyses.

Concentrations of TOC (Table S4) did not correspond to changes in wastewater tracers as TOC had with QACs concentrations in other studies (Doherty, 2013; Li and Brownawell, 2010). There were significant differences in samples collected before and after Hurricane Sandy: TOC concentration at sites WB12 (+39%) and WB24 (+69%) increased, where TOC concentrations at sites WB07 (−48%), WB11 (−36%), and WB26 (−27%) decreased. In most cases, these changes in TOC are not consistent with the changes observed in concentrations of wastewater tracers shown in Fig. 3 (Tables S2–S4). The greatest percent change in wastewater tracers pre- and post-Hurricane Sandy found in WB03 reflected the smallest change in TOC (−0.01%); however, the concentrations of TOC were 59,500 mg/kg (pre-storm) and 59,000 mg/kg (post-storm) were some of the highest observed from all HB samples (72nd and 68th percentile, respectively). The opposite was also observed at WB24, where the greatest decrease in median wastewater tracer concentrations also had the greatest increase in TOC concentrations (44,200 mg/kg to 74,700 mg/kg before and after Hurricane Sandy, respectively). The inconsistencies may be related to sediment redistribution in some portions of HB that were observed during the 2013 sample collection (for example, sandier sediment was observed in place of mud).

3.2. Interrelations among concentrations of wastewater tracers

Ratios of the fecal sterol 3-beta-coprostanol to cholesterol in sediment indicate variable sources of contaminants. Ratios greater than 0.2 have been used to indicate human fecal (sewage) sources (Furtula et al., 2012; Marvin et al., 2001; Grimalt et al., 1990). Concentration ratios were calculated for all 16 sites in the study and represent ranges of pre- and post-Hurricane Sandy within the bays and tributaries of HB (Fig. 5). Consistent with results shown in Fig. 3, ratios of 3-beta-coprostanol increased at both WB03 and WB26, with WB03 exhibiting a shift from non-human sewage sources in the pre-Hurricane Sandy sample to a human sewage source in the post-Hurricane Sandy sample (Fig. 5). The ratio of 3-beta-coprostanol also increased at WB12, which also has a large decrease in median (and overall) concentrations of wastewater tracers after Hurricane Sandy and highlights the complex nature of sediments and the use of a single tracer to describe the sources of contaminants to the sediment.

In addition to biochemical ratios indicative of sewage, relative concentrations of select PAHs in sediment can inform sources of PAHs in sediment. Comparisons of select PAHs have been used to help identify sources of wastewater containing petroleum (unburned) and petroleum-combustion products. Ratios of fluoranthene to fluoranthene plus pyrene (F/F + Py) and anthracene to anthracene plus phenanthrene (A/A + Ph) were calculated from concentrations in pre- and post-Hurricane Sandy samples (Fig. 5). Each of these ratios have been used in other studies to better understand potential sources of PAHs (Kanzari et al., 2014; Araghi et al., 2014; Yunker et al., 2002): sewage or coal combustion sources (F/F + Py > 0.5), petroleum combustion sources (0.5 > F/F + Py > 0.4 and A/A + Ph > 0.1), and unburned petroleum sources (F/F + Py < 0.4 and A/A + Ph < 0.1). Despite widespread inundation damage to vehicles, home heating oil tanks, and other petroleum storage units that resulted in spillage of untold amounts of petroleum to the bays on the south shore of Long Island (New York State Department of Environmental Conservation, www.dec.ny.gov/chemical/8437.html), only one site (WB03) exhibited a shift in the F/F + Py ratios into the range of unburned petroleum (Fig. 5). This suggests that wastewater and combustion sources were more dominant contributors to contaminated sediments than unburned petroleum sources following the storm. The shift in the F/F + Py ratio at WB03 was likely introduced via direct runoff or fuel oil spillage transported from the streets as floodwaters receded from the Mill River and Powell Creek watersheds. However, the A/A + Ph ratio does not reflect this shift at WB03 (Fig. 5). Thus, the sediment in the Mill River appears to reflect a combination of sewage inputs and the stormwater runoff from storm drains in the capture area; other studies have shown significant roadway contributions (i.e., elevated levels of heavy metals and PAHs) in the sediment north of the Bay Park STP (Hydroqual, 2013; Doherty, 2013). Most F/F + Py and all A/A + Ph ratios of paired samples exhibited little change in sediment PAH ratios between pre- and post-Hurricane Sandy samples and remained within the same source designation. This suggests that the combination of rain runoff and seawater inundation brought by Hurricane Sandy that flooded the streets and homes of the Mill River and Powell Creek watersheds, as well as Bay Park STP, and subsequently drained into the rivers and bays, did not change the dominant source of sediment bound PAHs distributed throughout HB.

In addition to evaluating ratios, correlation between select wastewater tracers (skatole, acetophenone, and anthracene), TOC, total androgens (summed concentrations of 4-androstene-3,17-dione, *cis*-androsterone, and testosterone), and total estrogens (summed concentrations of 17-beta-estradiol, and estrone) were evaluated to determine the extent to which compounds with sewage and (or) natural sources were present in the samples before and after the Hurricane Sandy. The tracers were plotted without regard to the date collected (though pre- and post-Hurricane Sandy samples were differentiated by symbol and color in plots) (Fig. 6). The Spearman rho value (a non-parametric correlation), is considered statistically significant at alpha = 0.05. For this study, a rho of 0.3 to 0.5 is considered moderately correlated, 0.5 to 0.7 is well-correlated, and >0.7 is very well-correlated. Spearman correlations were calculated to compare representative compounds with the highest frequency of detections above the reporting limit from each analytical method—wastewater-indicator (skatole, anthracene, and acetophenone), hormone (total androgens and 3-beta-coprostanol), and TOC. Other correlations between compounds of interest have been generated and can be found in Supplementary Material (Figs. S2–S6).

Comparisons of acetophenone to skatole (rho = 0.77) and to anthracene (rho = 0.84) shown in Fig. 6 indicates a very good correlation among these wastewater tracers. Because samples from both pre- and post-Hurricane Sandy are considered, the strong correlation between

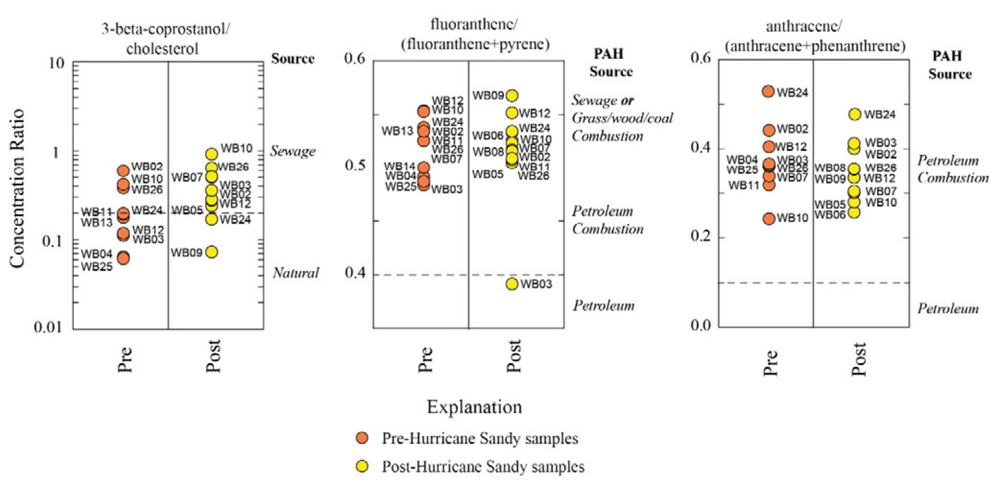

Fig. 5. Ratios of 3-beta-coprostanol to cholesterol, fluoranthene to fluoranthene plus pyrene and anthracene to anthracene plus phenanthrene for samples collected from Hempstead Bay, 2010–2013, from before and after Hurricane Sandy. Note: site names to the left of the dots are ones without a corresponding pre or post sample, site names to the right of the dots are those with both pre and post samples.

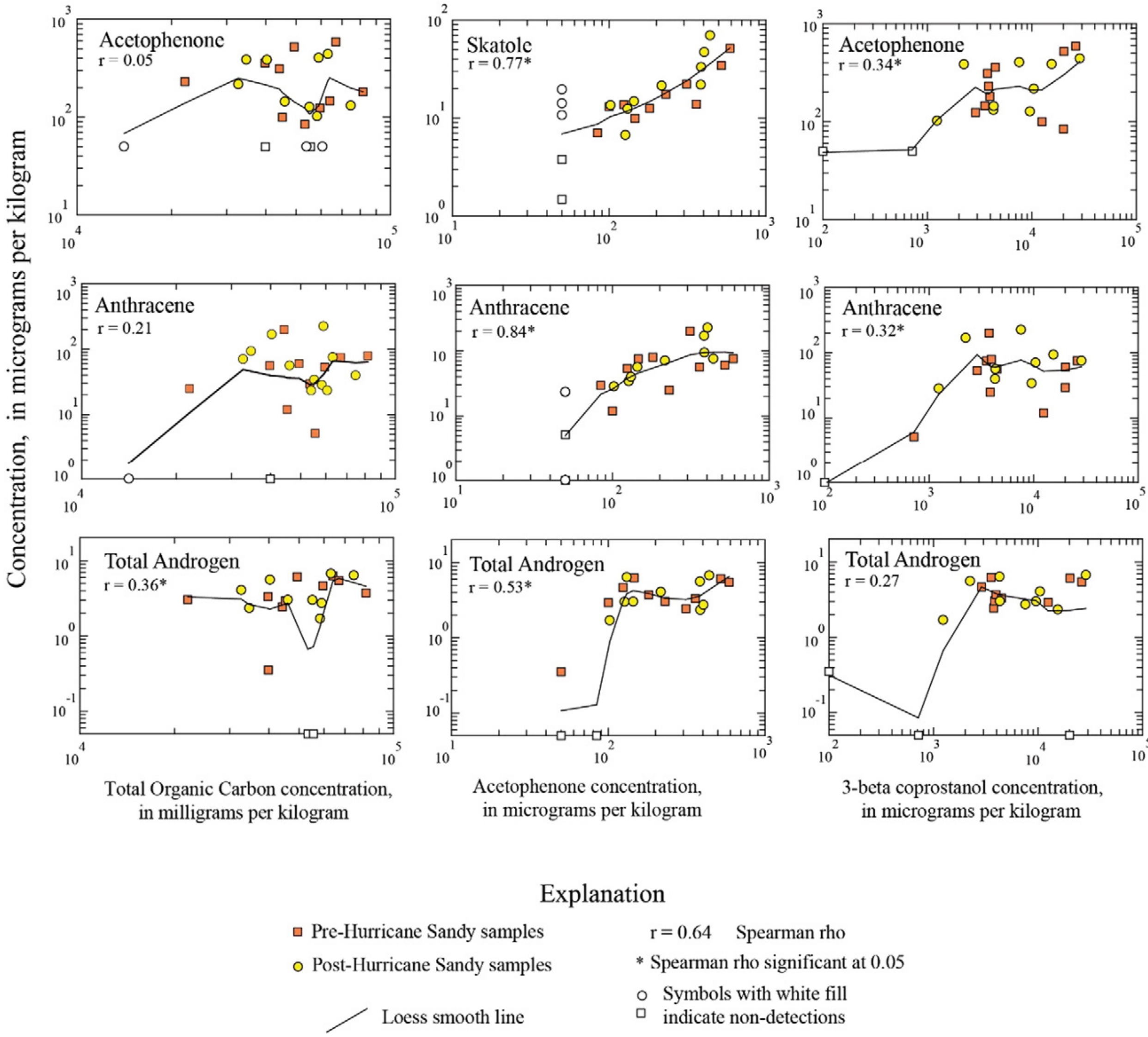

Fig. 6. Concentrations of total organic carbon, acetophenone, and 3-beta-coprostanol with select compounds for bed sediment samples collected in Hempstead Bay, 2010–2013, by pre- and post-Hurricane Sandy periods. Note that values for non-detects presented in Tables S2 and S3 were used to calculate statistics; however, the scale of the axes were optimized for detected values and thus may not show all non-detect values.

wastewater tracers suggests that these links are independent of degree of STP removal (e.g., skatole is typically well-removed during secondary treatment, and would be released at higher concentrations from an STP that has been disabled). Fig. 6 also depicts the overall poor correlation between both wastewater tracer and steroid hormone compounds measured in this study versus TOC. This is consistent with the TOC concentration change observed in pre- and post-Hurricane Sandy samples relative to the percent changes of wastewater tracers (Fig. 3) for reasons previously discussed. Only total androgens (rho = 0.36) provided a weak, but significant, correlation to TOC concentrations. The lack of correlation between wastewater tracers has been observed on a regional scale by Phillips et al. (2016–in this issue). Total androgens were only moderately correlated (rho = 0.53) to acetophenone. This lack of correspondence may reflect selective degradation of hormones in sediment (Tan et al., 2015).

Correlations among compounds assessed in this study to other sewage tracers, such as QACs, would provide additional diagnostic capabilities in determining sources. QACs have been used to identify degrees of treatment in wastewater-impacted sediment and determine the extent to which the sewage associated particles disperse from the discharge point (Doherty, 2013; Li and Brownawell, 2010; Li, 2009) and were found to have varying degrees of degradation and removal due to adsorption in STPs depending on chemical structure (Doherty, 2013; Clara et al., 2007). Future assessments and interpretations of data collected before and after Hurricane Sandy should focus on comparing QACs to the more traditional wastewater tracers presented in this study to better understand which areas were impacted by the discharge of poorly treated sewage and which areas show signs of sediment redistribution within HB.

4. Conclusion

Results from this study were useful in identifying areas of Hempstead Bay that had likely received additional sewage inputs from failed wastewater treatment infrastructure resulting from landfall of Hurricane Sandy. Bed sediment data from samples collected pre- and post-storm were analyzed to determine the concentrations of wastewater-related compounds at select locations. Data were examined in the context of relative changes among sites before and after the storm and observed changes in sediment distribution and TOC concentrations. In Mill River/East Rockaway Channel, the site just north of the Bay Park STP auxiliary outfall, increases in most wastewater tracers were detected, likely the result of sewage discharges to the Mill River from inundated sewer lines, stormwater runoff, and untreated sewage discharging from the auxiliary outfall. In Reynolds Channel, the sustained discharge of partially-treated sewage likely contributed to the increases in concentrations of wastewater contaminants observed adjacent to the Bay Park STP outfall. In Hewlett and Brosewere Bays, less change was observed and may have resulted from a combination of sediment redistribution and different hydrodynamics that affect the transport of effluent from Reynolds Channel and East Rockaway Channel to the back bays. In Middle Bay, decreases in concentrations of wastewater tracers at two near-shore sites likely reflect the redistribution of sediment, which resulted in less of a wastewater signature.

This study provides the first profile of wastewater tracer and steroid hormone compounds in bed sediment of HB. In general, correlations among tracers are strong in this study, particularly with skatole, anthracene, and acetophenone. However, correlation of TOC with wastewater tracers and steroid hormones was not as strong and was less predictable than with other sewage tracers (Doherty, 2013; Li and Brownawell, 2010). Steroid hormone data were only moderately correlated with select wastewater tracers when summarized by class (e.g., total androgens), and less among cholesterol and 3-beta-coprostanol, likely because of additional hormone inputs (from sources such as wildlife) and degradation of sewage-derived steroid hormones over time.

Findings from this study reinforce the importance of establishing a baseline of environmental data (in this case, sediment chemistry) ahead of a major weather event (e.g., major coastal storm) or predicted gradual change (e.g., sea-level rise) in vulnerable and critical coastal areas that may potentially experience any number of infrastructure failures. As there were a number of competing factors (i.e., emergency discharges, backed-up sewers, damaged STP infrastructure) before, during, and after Hurricane Sandy hit HB, it is not possible to discern the extent to which each contributed to the observed changes. In order to fully understand the degree to which each potential source of wastewater contamination contributes to changes in sediment quality in an estuary, it will be necessary to better understand infrastructure performance and weaknesses in response to these types of extreme events. Until these studies are performed and a baseline of sediment-quality exists within a routinely monitored network, it will not be possible to pinpoint and monitor infrastructure improvements (such as placement of check valves on outfalls and storm drains, and sewer main repairs) that are necessary to protect the ecological health of the adjacent estuary from being adversely affected by sewage-associated contaminants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.marpolbul.2016.03.044.

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